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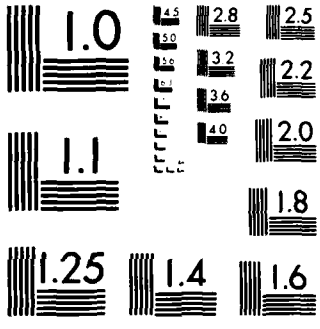

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An infrared study has been performed concerning the possible dissociation of CO_2 on supported Rh catalyst films. The data indicate that CO_2 does dissociate on Rh/TiO_2 and Rh/Al_2O_3 to form a carbonyl hydride species in accord with the work of Solymosi. This dissociation process is considerably enhanced by the presence of a small amount of hydrogen gas, but will proceed in the absence of hydrogen gas with the assistance of hydrogen migration from the support. Impurity boron also enhances the formation of the carbonyl hydride species, and hence CO_2 dissociation, when it is present in the supported Rh films.

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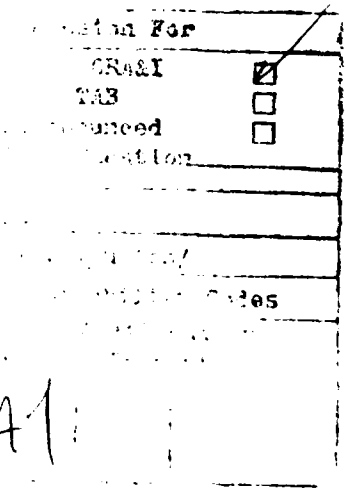

An Infrared Study of The Dissociation of Carbon Dioxide over Supported Rhodium Catalysts

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ABSTRACT

An infrared study has been performed concerning the possible dissociation of CO_2 on supported Rh catalyst films. The data indicate that CO_2 does dissociate on Rh/TiO_2 and Rh/Al_2O_3 to form a carbonyl hydride species in accord with the work of Solymosi. This dissociation process is considerably enhanced by the presence of a small amount of hydrogen gas, but will proceed in the absence of hydrogen gas with the assistance of hydrogen migration from the support. Impurity boron also enhances the formation of the carbonyl hydride species, and hence CO_2 dissociation, when it is present in the supported Rh films.

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The dissociation of carbon dioxide on rhodium, or lack thereoof, has become a very controversial topic, but one of great importance in methanation chemistry. Somorjai and coworkers have reported that CO_2 does dissociate on Rh foil and on several different Rh single crystal surfaces with high probability (ca. 10^{-1}) even at 300 K [1-5]. In those studies a variety of surface-sensitive techniques (TDS, LEED, and HREELS) were employed. However, Weinberg has recently questioned the results of Somorjai and coworkers based upon calculations employing available thermodynamic and kinetic data including an activation energy for the dissociation of CO_2 on clean Rh of 20.6 kcal/mol. He has suggested that the probability of dissociative adsorption of CO_2 on Rh is only 10^{-15} at low pressure and ambient temperature [6]. Somorjai [7] has rebutted the arguments of Weinberg by reviewing numerous literature references suggestive of CO_2 dissociation on Rh [8] and by using a corrected activation energy for the *CO/O associative reaction on* Rh [9] which entailed the use of an activation energy for dissociation of CO_2 on Rh of only 8.1 kcal/mol in his calculations and thus predicts a much higher probability of dissociation at 300 K than 10^{-15}. However Goodman and coworkers [10] have recently measured the activation energy for CO_2 dissociation on Rh(111) to be 17 kcal/mol and concluded that the probability of the dissociation process on Rh at 300 K and 760 Torr is only 10^{-11}. Very recently Solymosi and Kiss [11] have studied the adsorption and dissociation of CO_2 on Rh(111) and Rh foil using Auger, EELS, and TDS; they could find no evidence of CO_2 dissociation on clean Rh at 300 K. They did find dissociative chemisorption of CO_2 on Rh at 300 K when either H_2 or impurity boron was present [11]. The purposee of this letter is to report recent infrared findings from these laboratories concerning the dissociation of CO_2 on supported Rh catalysts as a part of an extensive study of CO_2 methanation.

The supported Rh catalysts used in this study were prepared as thin films on CaF_2 infrared windows by techniques employed here previously for infrared work involving CO adsorption on supported Rh [12-14] and the hydrogenation of CO over supported Rh[15]. For all of the work described here the Rh precursor salt was $RhCl_3 \cdot 3H_2O$. The support materials were alumina (Degussa Aluminum Oxide C, 100 m^2g^{-1}) and titania (Degussa Titanium Dioxide P25, 50 m^2g^{-1}). The gases employed (H_2, D_2, and CO_2) were of the highest purity obtainable from Matheson; the H_2 and D_2 were passed through liquid nitrogen traps before use. A Pyrex infrared cell similar to the one used here has been described previously [12-15]. All spectra were accumulated by a Perkin-Elmer 983 spectrometer operated at a resolution of 4.5 cm^{-1} at 2000 cm^{-1}. A Perkin-Elmer infrared data station facilitated data processing and storage.

Figure 1 shows the infrared spectra resulting from various sequential treatments of a 10% by weight Rh/TiO_2 film. The sample was heated to 460 K at 2×10^{-6} Torr for one hr and then reduced at 470 K by four successive doses of hydrogen at 70 Torr for time intervals of 5,5,10 and 20 min, each reduction cycle being followed by evacuation to 10^{-5} Torr. Then the sample was heated at 523 K for 16 hr at 2×10^{-6} Torr to remove as much hydrogen from the support as possible (complete removal is not possible at 523 K). A 12.6 Torr dose of CO_2 was then introduced into the infrared cell at 298 K and spectrum a in Fig. 1 was recorded immediately thereafter. Under these conditions no bands in the 2000 cm^{-1} region indicative of CO_2 dissociation to adsorbed CO species are evident. The bands at 1670, 1604, 1435, and 1221 cm^{-1} are indicative of the formation of carbonate and/or bicarbonate species on the support[16]. The sample was heated at 503 K for 4 hr; spectrum 1b was recorded after 30 min at 503 K, and spectrum 1c after the 4 hr heating period. A weak band developed near 2030 cm^{-1} during this heating cycle indicating the dissociation of CO_2 to some type of adsorbed

CO species. Then the sample cell was cooled to 298 K, evacuated, and dosed with 13 Torr of a 20:1 mixture of CO_2 and H_2. Spectrum 1d was immediately recorded at 298 K. Obviously the dissociation process is enhanced by the presence of the hydrogen gas as the 2032 cm^{-1} band doubles in intensity rapidly without heating. Spectrum 1e was recorded after only 30 min of heating at 503 K. The large intensity enhancement and shift to higher wavenumber (2038 cm^{-1}) of the CO band are indicative of increased coverage of the CO species on the Rh/TiO_2 surface, and hence to enhanced dissociation of CO_2 caused by the presence of H_2. A small band near 1893 cm^{-1} in spectrum 1e can be attributed to a bridged carbonyl species, either between two Rh atoms, or between a Rh atom and the support [12-15].

Experiments employing boric acid as a dopent were also conducted, typical spectral data being shown in Fig. 2. In these experiments ca. 4.9% by weight H_3BO_3 was added to the 10% Rh/TiO_2 sample slurry, and the mixture was sprayed onto a CaF_2 window in the usual fashion. The sample was subjected to the same reduction and heating process as used for the experiment discussed earlier (Fig. 1). Spectra a, b, and c in Fig. 2 have been reproduced from Fig. 1 for comparison. Spectrum 2d refers to the doped sample exposed to 12.9 Torr of CO_2 at 298 K. There are no bands in 2d which can be attributed to an adsorbed CO species; large new bands in the 1200-1500 cm^{-1} region must correspond to the reduced H_3BO_3 interacting in an undefined, complex manner with the support and possibly with the Rh. However, the important spectral development occurs upon heating to 503 K. The CO species having its band at 2030-2040 cm^{-1} again grows with time, and obviously at a greater rate than was the case for the undoped sample (spectra a,b, and c). Thus it would appear that the presence of the impurity boron species does enhance the dissociation of CO_2 over Rh/TiO_2 also, although not to as great an extent as does H_2. It should be noted that similar observations have been found here for 10% Rh/Al_2O_3 in the

presence of H_2 and H_3BO_3; however, the enhancement of CO_2 dissociation is more evident when TiO_2 is the support than for Al_2O_3.

Solymosi and coworkers have previously observed that H_2 enhances the dissociation of CO_2 over supported Rh catalysts [16]. They have also suggested that a carbonyl hydride may well be the species giving rise to the

low frequency CO band which they observed for Rh/Al_2O_3 at 2020-2039 cm^{-1}. We have also suggested that the carbonyl hydride species is an intermediate in the methanation of CO[15]. On the other hand, Iizuka and Tanaka [17] have concluded that this band is merely due to a linearly bound CO species at low coverage because they observed the same frequency with or without the presence of H_2. We agree strongly with the Solymosi interpretation. We have repeated the experiments discussed here using CO_2 and D_2. We obtain bands in the 2020-2040 cm^{-1} region of the <u>same intensities</u> under analogous conditions, but at lower frequencies by <u>ca.</u> 10 cm^{-1}, when D_2 is employed. This is consistent with a carbonyl deuteride species in that the isotopic substitution is two bonds removed from the CO moiety. The low frequency shift can not be attributed to lower CO coverage because the CO bands for the two experiments have the same intensity. One might wonder from where the carbonyl hydride arises which causes the weak band in spectra 1b and 1c given that no hydrogen gas was present in these experiments. We believe that the source of this hydrogen is the support material. Heating at 523 K and $2x10^{-6}$ Torr for 16 hr is just not sufficient to remove all hydrogen from the support. We have demonstrated this by producing HCD_3 and CH_2D_2, as well as CD_4, from a heated CO_2/D_2

mixture over Rh/TiO_2 pretreated by reduction in D_2[18]. The only possible source of H in this experiment was an "inverse spillover effect" from the support material. In other words, hydrogen migrates from the support to Rh to form the carbonyl hydride species. This process is more pronounced when TiO_2 is the support relative to Al_2O_3.

Our experiments on supported Rh catalyst films have also supported the findings of Solymosi and Kiss[11] as regards the enhancement of CO_2 dissociation on Rh by impurity boron. They suggested that the formation of a B-O surface species due to the strength of a B-O bond (787 kJ/mol) is the driving force for the dissociation process. Our results showed an enhancement of the carbonyl hydride IR band when boric acid was present. This probably means an increase in CO coverage to form the carbonyl hydride species because of enhanced dissociation of the CO_2 caused by impurity boron.

Unfortunately our results do not allow us to predict or calculate the probability of dissociation of CO_2 on Rh to help resolve the current controversy [1-7]. However, we have observed a carbonyl hydride species by infrared which could only result from the dissociatiion of CO_2 on Rh. furthermore, this process is enhanced by the presence of impurity boron, and greatly enhanced by the presence of H_2 gas such that dissociation occurs at 298 K when small amounts of H_2 are present. We suspect that the presence of either impurities or hydrogen is probably necessary for significant dissociation of CO_2 on Rh at ambient temperature and moderate pressure (eg. 10 Torr) of CO_2.

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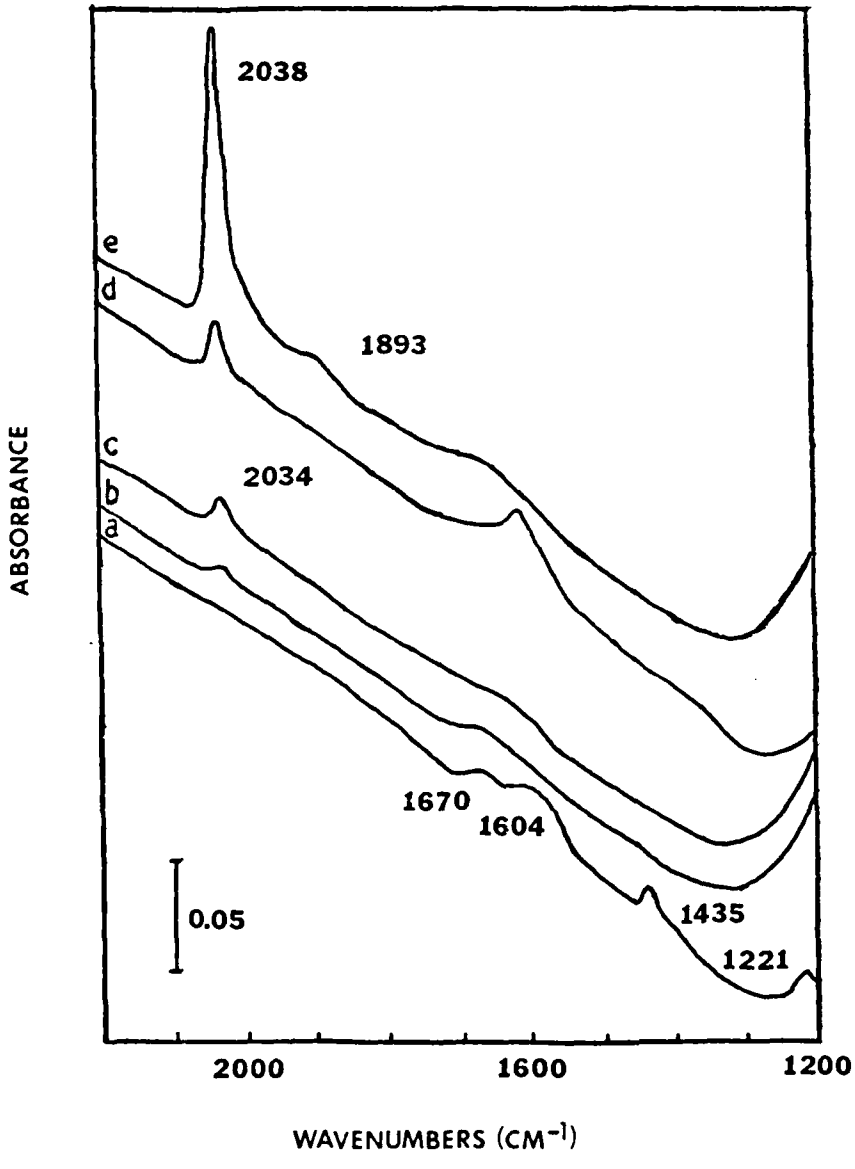
Figure Captions

Fig. 1 Infrared spectra of a 10% Rh/TiO_2 film (4.1 mg/cm^2) following reduction at 470 K, heating at 523 K for 16 hr at $2x10^{-6}$ Torr, and then: (a) introduction of 12.6 Torr CO_2 at 298 K, (b) heating at 503 K for 30 min, (c) heating at 503 K for 4 hr, (d) cooling to 298 K, evacuation, and introduction of 13.1 Torr of a 20:1 mixture of CO_2: H_2, (e) heating at 503 K for 30 min.

Fig. 2. Infrared spectra of a 10% Rh/TiO_2 film (4.5 mg/cm^2) doped with 4.9% H_3BO_3 following reduction at 470 K, heating at 523 K for 17.75 hr at $2x10^{-6}$ Torr, and then: (d) introduction of 12.9 Torr CO_2 at 298 K, (e) heating at 503 K for 30 min, (f) heating at 503 K for 4 hr. Spectra (a)-(c) are those shown in Fig. 1 for a film free of H_3BO_3.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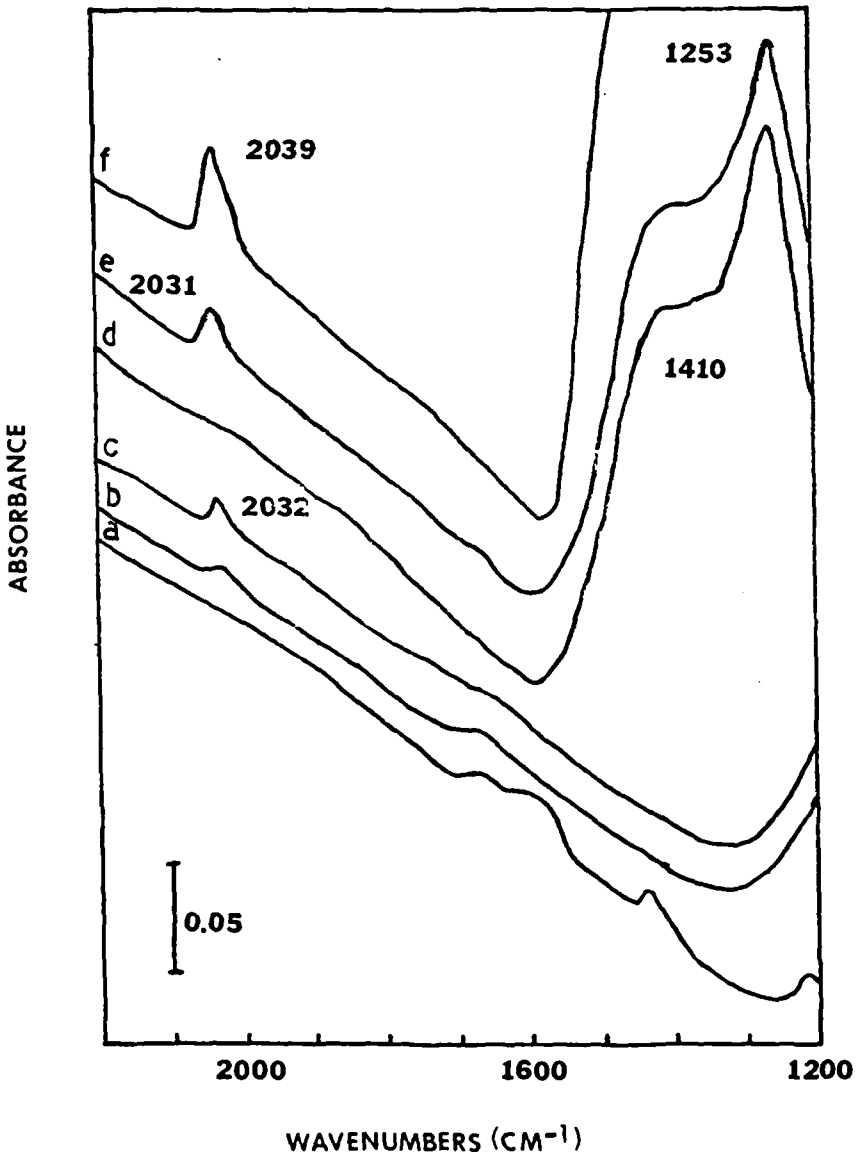
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